Uncertainty Analysis of Reactivities of Alternative-Fueled Vehicle Emissions

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Objective

Urban ozone (O_3) reduction strategies that target reactive organic gases (ROGs) have focused primarily on controlling the total mass of ROG emitted, and have neglected the variation in potential for O_3 formation by individual species. Analysis of the air quality impact resulting from organic species is important for identifying effective strategies and is central to the recent Clean Fuels and Low Emission Vehicle regulations in California, particularly regarding quantifying reactivity adjustment factors (RAFs) for application to alternative fuels.

The objective of this study is to quantify reactivity scales and RAFs using comprehensive modeling methods, and to examine the uncertainty in these scales caused by the chemical mechanism rate constants and product speciation parameters.

Approach

A detailed version of the Statewide Air Pollution Research Center (SAPRC90) chemical mechanism was integrated into the California Institute of Technology (CIT) model (a three-dimensional, Eulerian, photochemical air quality model) and a one-dimensional, photochemical model. Three-day episodes for Los Angeles were simulated with the CIT model, and 10-hour episodes for a general urban atmosphere with the one-dimensional model. These simulations were used to quantify the response of O_3 and other pollutant concentrations to increases in emissions of 26 ROGs and carbon monoxide (CO). Reactivity metrics were developed to examine the response of peak O_3 and various exposures to these emissions changes.

Nine rate constant sets were shown through Latin Hypercube Sampling with the one-dimensional model to contribute approximately 80% of the total uncertainty in species reactivity. Uncertainty analysis was then performed with the CIT model on these sets to examine the effects on RAFs of 2σ changes. The effects of 2σ changes on product speciation will also be examined using the same approach.

Accomplishments

The resulting reactivity scales showed general agreement with the maximum incremental reactivity (MIR) scale. Some interesting differences in values for photolytic species, such as a lower formaldehyde reactivity, were observed. Variation in relative reactivities over all species and simulations averaged about 14% in response to the 2σ changes in rate constants.

Results from both models indicate that among the rate parameters in the SAPRC mechanism, the principal targets to improve confidence in reactivity calculations should include the parameters associated with peroxyacetyl nitrate (PAN) chemistry, hydroxy radical (OH) rate constants, photolysis rates for critical organic compounds,

and further characterization of conditions affecting photolysis rates. However, results from both models indicate that the influence of rate parameter uncertainties on calculated RAF values is generally small.

Future Direction

The results of this study have many possible ramifications for the use of reactivity scales in a regulatory framework, particularly in evaluating the air quality impacts of alternative fuels. Important uncertainties were identified for further refinement. Current research on this project is directed at evaluating uncertainties in product yields and their effects on O_3 prediction for RAFs.

Publications

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